

# Phase Segregation in Two-dimensional Polymer Blend Films

D. Winesett and H. Ade (North Carolina State U.)

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Beamline(s): X1A

**Introduction:** The physics of two-dimensional binary fluids is a complex and fascinating subject that has received considerable computational and theoretical treatment for years but still lacks somewhat in experimental verification. It is widely believed that, after initial phase segregation, domains are expected to grow with a well defined and scaling invariant growth exponent  $[R(t) \sim t^\alpha]$  where  $\alpha$  is dependent on the coarsening mechanisms present. Several values of  $\alpha$  have been predicted, including diffusion driven growth ( $\alpha=1/3$ ) and hydrodynamic growth ( $\alpha=2/3$ ). Recent lattice-Boltzmann simulations [1] indicate a breakdown of this scaling invariance due to the competition between these growth mechanisms.

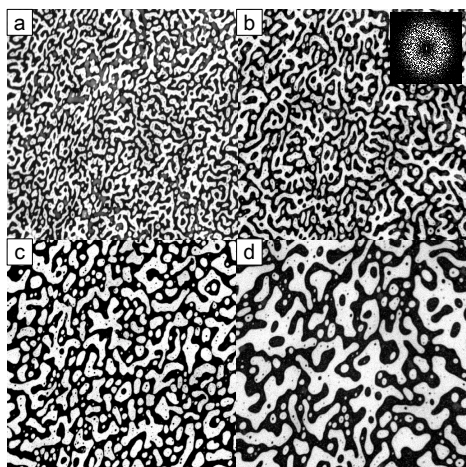
**Methods and Materials:** We are examining these phenomena using polymer blend films of low molecular weight (10,000 and 21,000 g/mol) monodisperse ( $M_w/M_n=1.02$ ) polystyrene (PS) and poly(methyl methacrylate) (PMMA). Polymer blends are ideal to examine phase segregation phenomena due to their slow dynamics and the relative ease at which the important physical parameters, such as viscosity, diffusivity, and miscibility, can be varied by altering the chemical composition of the blend constituents. Symmetric blend films are spun-cast onto  $\text{Si}_3\text{N}_4$  windows that have been rendered energetically neutral with a P(S-*ran*-MMA) copolymer treatment. Films are then annealed at 175°C in a vacuum oven ( $10^{-3}$  Torr) for various times to initiate phase segregation and then examined with Scanning Transmission X-ray microscopy (STXM) at the X1A beamline of the NSLS.

**Results:** As an example of our recent results, **Figure 1** shows quantitative PS maps from identically prepared symmetric 21,000 g/mol blends with a thickness of 132 nm (determined with ellipsometry). Samples were annealed for a) 15 minutes, b) 1 hour, c) 3 hours and d) 18 hours. The development of segregated domains appears to be scaling invariant. Small, rounded domains are growing over time within a partially co-continuous network, which also develops, with time. In order to quantify this domain growth, we measure characteristic lengthscales by calculating the inverse first moment of the circularly averaged structure factor of each image (For example, see inset of Figure 1B) and plot this vs. annealing time in an ln-ln plot. Preliminary results indicate a smaller than expected, but remarkably consistent growth exponent of  $\alpha=1/4$ . Four separate annealing sequences with different molecular weights and sample thicknesses exhibit this behavior. To the best of our knowledge, this is the only experimental work, which reveals this growth behavior [several numerical simulations predict it, most recently ref [2]].

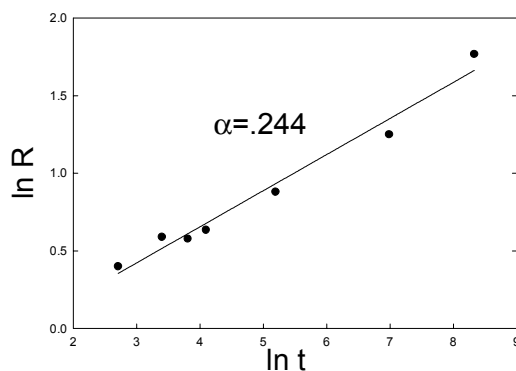
**Conclusions:** Two-dimensional domain growth in low molecular weight polymer blends develops with a smaller exponent than theoretically expected. Further experiments at the NSLS will attempt to better understand and elucidate the mechanisms present in these systems.

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**References:** [1] A. Wagner and J. Yeomans, "Breakdown of Scaling Invariance in the coarsening of Phase-Separating Binary Fluids," *Phys. Rev. Lett.* **80** 1429 (1998). [2] C. Castellano and F. Corberi, "Pinning of Phase Separation in a Model of Binary Polymer Blends," *Phys Rev. E* **61**(3) 3252 (2000).



**Figure 1.**  $30 \mu\text{m}^2$  PS maps from symmetric blend films annealed at for a) 15 minutes, b) 1 hour, c) 3 hours, d) 18 hours. White = PS, dark = PMMA. Inset =  $|\text{FFT}|^2$  of Figure 1B.



**Figure 2.** Log-log plot of domain size vs. time for series of 21,000 g/mol, 125 nm thick films.